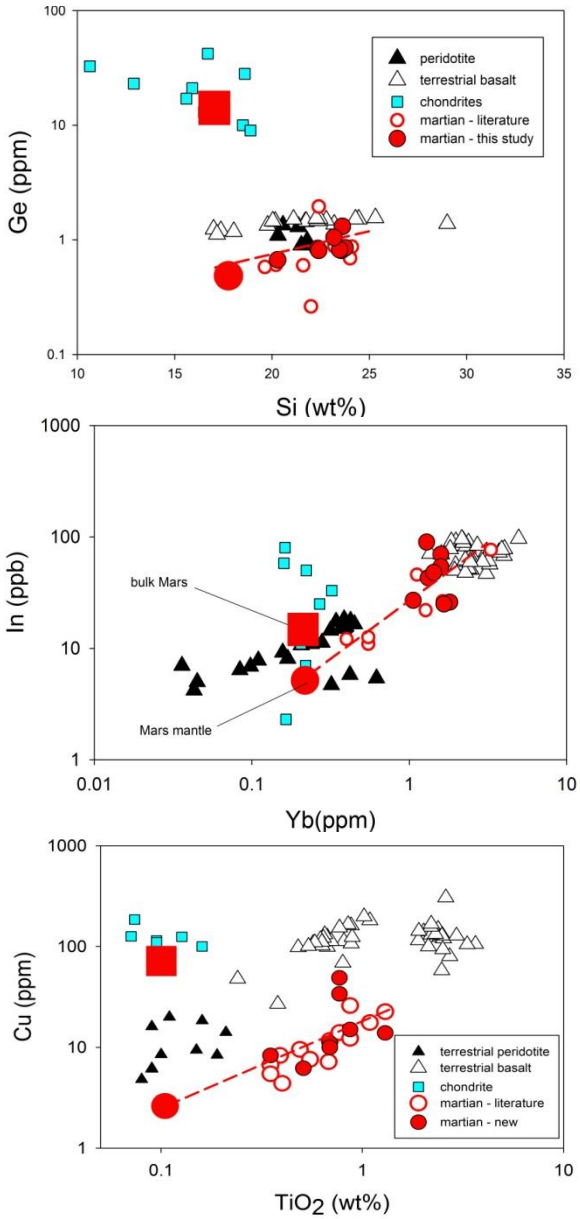
VOLATILE SIDEROPHILE ELEMENTS IN SHERGOTTITES: CONSTRAINTS ON CORE FORMATION AND MAGMATIC DEGASSING. K. Righter[1] and M. Humayun[2], [1] Mailcode KT, NASA-JSC, 2101 NASA Pkwy., Houston, TX 77058 (kevin.righter-1@nasa.gov); [2]Dept. of Earth, Ocean & Atmospheric Science, and National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL 32310 (humayun@magnet.fsu.edu).

Introduction: Volatile siderophile elements (e.g., As, Sb, Ge, Ga, In, Bi, Zn, Cd, Sn, Cu, Pb) can place constraints both on early differentiation as well as the origin of volatiles. This large group of elements has been used to constrain Earth accretion [1,2], and Earth-Moon geochemistry [3]. Application to Earth has been fostered by new experimental studies of these elements such as Ge, In, and Ga [4,5,6]. Application to Mars has been limited by the lack of data for many of these elements on martian meteorites. Many volatile elements are considered in the pioneering work by [7] but for only the small number of martian samples then available. We have made new measurements on a variety of martian meteorites in order to obtain more substantial datasets for these elements using the analytical approach of [8]. We use the new dataset, together with published data from the literature, to define martian mantle abundances of volatile siderophile elements. Then, we evaluate the possibility that these abundances could have been set by mid-mantle (14 GPa, 2100 ºC) metal-silicate equilibrium, as suggested by the moderately and slightly siderophile elements [9]. Finally, we examine the possibility that some elements were affected by volatility and magmatic degassing.

Analytical Methodology: Polished sections of 6 martian meteorites (Shergotty, Zagami, Los Angeles, EETA 79001A, Y-000097, and Y-980459) were analyzed for 73 elements by UP193FX excimer laser ablation system coupled to a Thermo Element XR at the Plasma Analytical Facility, FSU [8]. Spot sizes of 100 µm, rastered over the surfaces at 25-50 µm/s, for areas ranging from 3-24 mm^2 were used. All elemental peaks were collected in low resolution using triple mode detection. Standards used included NIST SRM 610, USGS glasses BCR-2g, BHVO-2g and BIR-1g.

Element correlations: Correlations of siderophile elements with lithophile elements of similar compatibility in igneous fractionation processes have been used to estimate mantle abundances in differentiated bodies for which we have not direct mantle samples (e.g., [10]). Here we examine the Ge-Si, In-Yb, and Cu-Ti pairs chosen based on previous work ([1,7]). Correlation of W-Ta, Zn-Ti, and Cd-Yb are also used below but not shown here. Terrestrial examples are shown for comparison (Figs 1-3). For Ge, the terrestrial peridotites fall just below the trend formed by terrestrial basalt, and as a result the martian mantle



Figures 1,2,3: Ge-Si, In-Yb, and Cu-TiO_2 correlations for terrestrial peridotite, basalt, chondrites and martian basalt (shergottites) illustrating estimated martian mantle concentrations for each siderophile element. Red square is the bulk Mars composition of [11]; large red circle is the martian mantle estimate using the correlations among shergottites, with guidance from terrestrial mantle-basalt trends. Data from [1,4, 7,16,19-24] and this study.

estimate is placed just below the shergottite basalt trend. For In, the spread in terrestrial mantle data is large, making the slope for the Earth more uncertain, but mimicking either a shallow or steep trend for martian samples results in little or no depletion of In in the martian mantle. Finally, Cu shows a significantly larger depletion relative to the terrestrial peridotite and basalt. Our new W data help better define the W depletion derived by [9]. New Zn data indicate little to no depletion of Zn in the martian mantle, and Cd (like Cu) is depleted more in the martian mantle than in the terrestrial mantle.

Core-mantle partitioning: Righter and Chabot (2011) [9] proposed that the abundances of Ni, Co, Mo, W, V, Cr, P, and Ga were set by an intermediate depth magma ocean at 14 GPa and 2100 ºC. The newly defined mantle depletions of the volatile siderophile elements can be evaluated with respect to this model. Using the bulk Mars composition of [11] along with a 22 mass % core with Xs = 0.17, we can calculate what D(met/sil) would be required to explain the above derived mantle abundances. These calculations account for depletion due to volatility, as did [9] for Ga and P.

For Cu and Ge, the predictive expressions of [12] and [4], respectively, can be used to calculate mantle abundances of 1.5 ppm (D(Cu) = 120) and 0.3 ppm (D(Ge) = 100), close to the values from the element correlation of 3.0 ppm and 0.7 ppm. Zn and In both require D<0.1, and the high PT datasets of [13] and [5] both indicate these low values are highly possible for the PT conditions of [9]. Although there are not systematic partitioning data available for Cd, the D(Cd) required is 3, similar to a metal/silicate D(Cd) = 1.9 determination by [14]. Whether this depletion can be explained solely by core formation should be tested with future high PT metal/silicate partitioning for Cd. It appears as if these five elements are also consistent with an intermediate depth magma ocean on Mars.

Magmatic degassing: It is not known whether shergottites have degassed and if so to what extent [15]. Many of the volatile siderophile elements could be susceptible to loss to volcanic gas during degassing [16]. Norman et al. (2004) [16] have shown that elements such as Re and Cd are more significantly lost than others such as Zn and Cu. Subsequently, the Cu/Re and Cd/Dy ratios may yield information about how much of these elements may have been lost during magmatic degassing [16]. Terrestrial volcanic gases are most commonly dominated by H-C-O-S gases, but on Mars Cl is also a significant gas component, and Cl-bearing melts and gases can promote the mobility of many elements including Cd and Re [18]. Examination of Cu/Re vs S trends in Hawaiian glasses illustrates the degassing trend of [16], and some portion of the martian sample data may indicate degassing. Similarly, for Cd/Dy vs. S there is a comparable decrease in Cd/Dy as there is in the Hawaiian suite, suggesting degassing may play a role. We will examine more elements and try to place constraints on how much degassing could have affected elemental abundances of these elements.

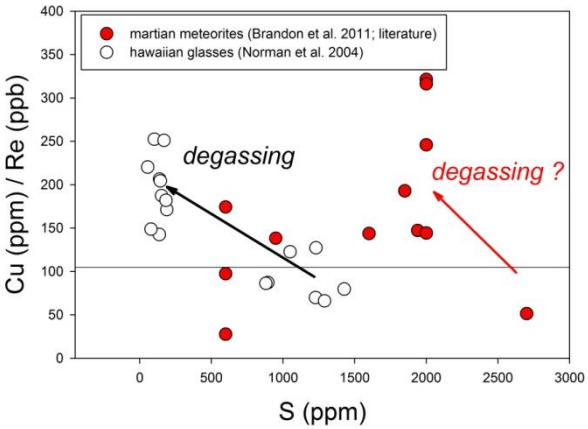


Figure 4: Cu/Re vs. S (ppm) for Hawaiian glasses [16] compared to martian basalt (Re data from [17] and Cu and S data from [19]). These trends have been corrected for fractionation which may lower Dy, and increase Cu, Re, and Cd with degree of evolution.

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